# A METHOD FOR SAMPLING AND DETERMINING CHLOROPICRIN IN AIR

by

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HS-1083 June 30, 1983

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## SUMMARY

A method was developed for the determination of chloropicrin in air. This method is designed to collect samples for 40 minutes, trapping chloropicrin on XAD-4 resin sampling tubes drawn by portable air sampling pumps operating at 200 mL/min. Recovery of chloropicrin was 90 percent from sampling tubes fortified at a level of 2 ug, with samples desorbed using ethyl acetate. Extracts were analyzed by capillary column gas chromatography, with a minimum detectable level of 1 ppb in field samples. Recommendations are made for further research to increase the versatility and the validity of this method. The results of this study are preliminary, but indicate that a sampling method for chloropicrin is achievable.

## INTRODUCTION

Chloropicrin (trichloronitromethane) is a colorless, slightly oily liquid which is miscible in many organic solvents and has a vapor pressure of 20 mm Hg at 20°C.[1/] In California, it is used as a stored commodity fumigant, a soil fumigant by itself or in conjunction with methyl bromide, and a warning agent for the presence of methyl bromide during structural fumigation. In 1981, reported use of chloropicrin as a fumigant in California was over 1.4 million pounds.[2/] Chloropicrin is a lacrymating agent, and a severe respiratory and skin irritant.[3/] Chloropicrin is severely irritating to the eyes at concentrations of 0.3 ppm. For prevention of eye irritation and to insure against eventual pulmonary changes, the American Conference of Governmental Industrial Hygienists (ACGIH) recommends a threshold limit value (TLV) of 0.1 ppm with a short-term exposure level (STEL) of 0.3 ppm.[1/]

Concerns have been raised about the hazards of chloropicrin exposure to people living adjacent to fumigated fields. In Orange County, California, agricultural fields are commonly intermingled with housing. In years past, the county agricultural department has received complaints from persons living near fumigated fields who experienced symptoms of eye irritation, respiratory tract irritation and headaches. It is not known if chloropicrin exposure is related to these occurrences, however, it can be hypothesized that, during atmospheric inversions, levels of chloropicrin build up and drift.

The Worker Health and Safety Unit was asked to collect air samples to determine if irritating levels of chloropicrin could drift from fumigated fields. A review of the literature did not reveal any studies of chloropicrin exposure, or any methods for determination of chloropicrin in air. Therefore, it became necessary to develop methods for sampling and analyzing chloropicrin in air. The following is a brief report of the methods development in progress, with recommendations for areas of further study.

## MATERIALS AND METHODS

Collection and Recovery Studies. Collection efficiencies of the solid adsorbents silica gel and XAD-4 resin were evaluated. Commercially prepared sampling tubes were obtained from SKC, Inc. (Catalog numbers 226-15 silica gel and 226-30-11-04 XAD-4 tubes.) Determination of collection efficiencies were made with an apparatus consisting of a glass U-tube connected with Tygon tubing to a sorbent tube and an MSA model C-210 battery powered air sampling pump.[4/] Chloropicrin standards dissolved in ethyl acetate were injected with a microliter syringe onto a small plug of glass wool previously inserted into the mouth of the U-tube. The sampling pump was operated for 40 minutes at 200 mL/min air flow across the sorbent bed (calibrated with a bubble tube), corresponding to a total sample volume of 8 L. Each adsorbent was evaluated at levels of 20 ppb and 200 ppb, with one trial performed at each level (see Table I). Based on these preliminary trials, XAD-4 was selected for use in field sampling.

Desorption efficiency was determined only for XAD-4. This was done by scoring and breaking the sampling tube and injecting chloropicrin standard into the front sorbent section using a microliter syringe. The sampling tube was sealed with the supplied plastic caps and allowed to stand at room temperature for a few hours before desorption. The desorption efficiency was 90 percent at a level of 2 ug/sample.

Analysis. Samples were prepared for analysis by scoring and breaking the tubes and removing the retaining wire. The inlet glass wool, front sorbent section and polyurethane foam separator were placed in a 5 mL vial containing 4 mL nanograde ethyl acetate. The backup resin section was placed in an identically prepared vial. The vials were sealed with Teflon lined screw caps and samples were desorbed by rotating the vials for one hour. Extracts were analyzed by capillary column gas chromatography using a Hewlett-Packard 5880 chromatograph with an electron capture detector. The column was a 30 m by 0.25 mm fused silica coated with 0.25 um J & W 1701, operating at a 100:1 split ratio. Column pressure was 20 psi and the split flow was 40 mL/min.

Carrier gas was helium and the detector make-up gas was argon-methane. Operating temperatures were 220°C for the split injector liner, 40°C for the column, and 300°C for the detector. Under these conditions, chloropicrin eluted in 6.5 minutes. Instrumental sensitivity was 0.03 ug/sample.

Field Use Description. Preplant soil fumigations with methyl bromide and chloropicrin are performed year round in California, with a peak use period from July to October. Methyl bromide and chloropicrin are formulated together. The fumigants are commercially available in pressurized cylinders, and during the applications monitored, were applied by shank injection into the soil to a depth of eight inches using a positive pressure closed system (pressurized with nitrogen gas). A one mil polyethylene tarp is mechanically laid over the soil, the tarp laying mechanism located immediately behind the shanks. The tarp slows dissipation of the gases into the atmosphere, thus improving the efficacy of fumigation. Fumigant application rates for open field injection are commonly 325 to 375 pounds (of formulated product) per acre, depending upon the crop being planted.

Sampling Methods. Breathing zone samples were collected from employees performing preplant fumigations of strawberry fields in Orange County, California, in September 1982. Based on results from the collection studies, the sampling train consisted of two XAD-4 resin tubes connected in series by a short length of Tygon tubing. The sampling train was connected with Tygon tubing to a MSA Model C-210 personal sampling pump. Pumps were calibrated with a bubble tube prior to use, to draw approximately 200 mL/min across the resin bed; thereafter, flows were determined by the pump counters. Sampling durations were approximately 45 minutes, yielding sample volumes ranging from 7.3 to 10.4 L. After sampling, the tubes were separated, capped with the supplied plastic caps, frozen on dry ice, and transported to the analytical laboratory. Analyses were completed within seven days of sampling.

Each sample was analyzed in three sections to determine potential for chloropicrin breakthrough. The entire upstream sample tube was analyzed as the "front section." The downstream sample tube was divided into a "back section" and "second back section". (See Figure 1.)

## RESULTS

Results from the laboratory collection efficiency studies are in Table I. Determination of breakthrough in the laboratory samples are in Table II. Levels of chloropicrin found in employee breathing zone samples collected in the field are listed in Table III. Determination of trapping efficiency in the field samples are in Table IV. Ethyl acetate washes of the U-tube following each collection trial had no detectable levels of chloropicrin. Analyses of the second back sections of field samples showed no detectable levels of chloropicrin.

## DISCUSSION

Collection efficiency and breakthrough of chloropicrin was acceptable for the XAD-4 low level spike, but not for the high level spike. Results from this study indicated that breakthrough of chloropicrin was excessive in silica gel. It is not apparent why XAD-4 performed so poorly in the laboratory studies at the high level. One possibility is that chloropicrin adsorbed as a 10.9 ug "plug" which locally overloaded the sorbent in a particular zone, allowing a greater fraction of chloropicrin to desorb into the vapor-state, which would elute chromatographically through the sorbent bed. In the field samples, a lower concentration per unit time of chloropicrin would be presented to the sorbent, allowing slower migration through the sorbent bed. The rationale behind using sorbent tubes in series was that a longer sorbent bed would minimize potential breakthrough. Also, the attempt was made to hold sample volumes to 10 L to minimize breakthrough.

Minimal breakthrough of chloropicrin was observed in the field samples. Trapping efficiency, as measured by percent of the total sample collected on the front section of the sampling train, was greater than 90 percent. (See Table IV.) Since chloropicrin was not detected in the third section of the sampling train, in any of the field samples, this can be accepted as evidence that quantitative trapping was achieved. Air sampling results in Table III were calculated only from chloropicrin trapped on the front section of the sampling train, and are corrected for 90 percent recovery.

Midway through this study, it came to our attention that the National Institute of Occupational Safety and Health (NIOSH) failed to develop and validate a sampling method for chloropicrin.[6/] The NIOSH study evaluated several solid sorbents, including charcoal, silica gel, XAD-2 and Tenax-GC. Tenax-GC was considered to give the best desorption efficiency, even for small (3 L) sample sizes. XAD-2 resin produced acceptable recoveries with desorption after one day, however with seven days storage, recoveries were 45

percent. The report did not specify storage conditions. Concerning XAD-2 resin, the investigators recommended immediate desorption of samples after collection to alleviate sample instability in storage.

Chloropicrin levels detected in employee breathing zone samples ranged from less than 1 ppb to 181 ppb. Employees were not interviewed to determine whether exposure levels correlated with the occurrence of any symptoms.

More determinations of collection and desorption efficiencies should be performed to determine the coefficient of variation for sampling and analysis. The occurrence of breakthrough, especially at higher levels should be investigated more fully. The stability of chloropicrin during sample storage should be examined, especially in light of the results of the NIOSH study. The selection of 10 L as the maximum sample volume is empirical, and could possibly be enlarged. Long-term sampling could be performed by using a lower flow rate (less than 50 mL/min), and should be investigated. Numerous questions remain to be answered and further testing must be done before this method can be considered reliable. It should be determined if special sample handling, storage requirements or quality control measures are necessary. However, the results from this limited study indicate that a sampling and analytical method for determining chloropicrin in air appears achievable.

TABLE I

Collection Efficiencies of Silica Gel (SG) and XAD-4 Resin for Chloropicrin

| Sorbent[a] | Simulated Level In Air (in ppb based on 8 L) | Chloropicrin Applied (ug) | Chloropicrin Trapped (ug) | Trapping Efficiency (Percent) |
|---|---|---|---|---|
| XAD-4 | 20 | 1.09 | 0.91 | 83.5 |
| XAD-4 | 200 | 10.90 | 7.44 | 68.2 |
| SG | 20 | 1.09 | 0.86 | 78.8 |

[a] Silica gel was not evaluated at 200 ppb level due to high breakthrough at the low level spike (see Table II). Each result is of a single sorbent tube.

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TABLE II

Determination of Chloropicrin Breakthrough in Laboratory Spiked Samples

| Sample | Total Micrograms Trapped on Entire Sorbent Tube | Total Micrograms Found in Front Sorbent Section | Percent Breakthrough |
|---|---|---|---|
| XAD-4, 20 ppb | 0.91 | 0.79 | 13.2 |
| XAD-4, 200 ppb | 7.44 | 5.91 | 20.6 |
| SG, 20 ppb | 0.86 | 0.29 | 66.3 |

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TABLE III

Chloropicrin Levels Detected in the Breathing Zones of Employees Performing Soil Fumigations (Field Samples)[a]

| Job Type | Chloropicrin Detected ppb | Chloropicrin Detected $mg/M^3$ |
|---|---|---|
| 1 Driver | 106 | 0.7 |
| 2 Copilot | 96 | 0.6 |
| 3 Driver | 47 | 0.3 |
| 4 Copilot | 26 | 0.2 |
| 5 Driver | 43 | 0.3 |
| 6 Driver | 80 | 0.5 |
| 7 Copilot | ND[b] | ND |
| 8 Driver | 126 | 0.9 |
| 9 Copilot | 181 | 1.2 |
| 10 Shoveler | 45 | 0.3 |

[a] Sampling durations were all approximately 40 to 45 minutes.

[b] Chloropicrin not detected, minimum detectable level 1 ppb.

TABLE IV

Determination of Chloropicrin Trapping Efficiency in Field Samples

| | Micrograms Found on Front Section | Micrograms Found on Back Section[a] | Trapping Efficiency (percent) |
|---|---|---|---|
| 1 | 6.28 | 0.128 | 98.0 |
| 2 | 5.27 | 0.173 | 96.7 |
| 3 | 2.58 | 0.067 | 97.4 |
| 4 | 1.33 | ND[b] | 100.0 |
| 5 | 2.29 | 0.038 | 98.4 |
| 6 | 5.05 | 0.077 | 98.5 |
| 7 | ND | ND | -- |
| 8 | 5.58 | 0.030 | 99.5 |
| 9 | 9.47 | 0.032 | 99.8 |
| 10 | 2.43 | 0.030 | 98.8 |

[a] No chloropicrin was detected on the second back sections of any air samples. (See Figure 1.)

[b] Means none detected, minimum detectable level is 0.03 micrograms.

## References


1. American Conference of Governmental Industrial Hygienists. Documentation of the Threshold Limit Values, 4th Edition (1980).

2. California Department of Food and Agriculture. 1981 Annual Pesticide Use Report.

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4. United States Environmental Protection Agency. Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples. EPA-600/8-80-038 (1980).

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6. National Institute of Occupational Safety and Health. Failure Report, Chloropicrin, Method No. S-212, in Manual of Analytical Methods, Volume 7, page xiii (1982).

Figure I

Schematic representation of the sampling train for chloropicrin.